X-Ray Diffraction and Melting-Point Data on Some Binary Mixtures of Trans-6 Through 12-Octadecenoic Acids and Their Dihydroxystearic Acids[1]

DANIEL SWERN,[2] LEE P. WITNAUER,[2] S. A. FUSARI,[3] and J. B. BROWN,[3] Eastern Regional Research Laboratory,[4] Philadelphia, Pennsylvania, and Ohio State University, Columbus, Ohio

X-RAY DIFFRACTION and melting-point data on the pure *trans*-6- through 12-octadecenoic acids and the corresponding dihydroxystearic acids have recently been reported (2-6). In this note we wish to describe the results of similar work on some binary mixtures of the *trans* acids and of the dihydroxystearic acids. This work was done as part of a program on the identification of compounds which are isolated from autoxidation, hydrogenation, and isomerization studies on long-chain compounds.

Experimental

Starting Materials. *Trans*-6-, 7-, 8-, and 11-octadecenoic aiids were prepared by the procedures of Fusari, Greenlee, and Brown (2). *Trans*-9-octadecenoic acid (elaidic acid) was prepared from oleic acid by isomerization with powdered selenium at 220° (8). The high-melting dihydroxystearic acids were prepared from these acids by hydroxylation with hydrogen peroxide in formic acid solution (2, 7). The low melting dihydroxystearic acids were similarly prepared from the *cis*-isomers.

X-Ray Technique. This has already been reported (9). In order to obtain the materials in a suitable crystalline state, the unsaturated acids were dissolved in acetone and the solutions were evaporated to dryness under a stream of nitrogen; ethanol was employed with the dihydroxystearic acids.

Melting Points. These were determined by the capillary method, employing samples which had been prepared for x-ray examination as described in the preceding paragraph. Within the melting range the temperature was raised at a rate not exceeding 0.25° per minute.

Results and Discussion

Table I summarizes the results obtained on the pure acids. The agreement between our results and the published ones are, in general, extremely good.

Table II summarizes the results obtained on 50:50 binary mixtures. All binary mixtures of *trans*-octadecenoic acids show marked depressions in melting point, but whether the melting range is narrow or wide depends on the components of the mixture. Mixtures of even-even (these refer to the number designating the position of the double bond) or odd-odd acids show marked depressions but narrow ranges (usually 1-1.5°) whereas mixtures of odd-even acids show broad melting ranges (usually 5-6°). The x-ray

TABLE I

Melting Point and X-Ray Diffraction Data on Pure Acids

Trans-Octadecenoic Acid			High-Melting Dihydroxystearic Acid[a]			Low-Melting Dihydroxystearic Acid[b]		
	M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å
6-	52.7-53.4	44.9	6, 7-	122.8-123.3	45.2	6, 7-	114.0-115.0	45.4[3],44.4[5]
7-	43.7-44.1	49.0	7, 8-	132.7-133.0	41.8[c]	7, 8-	95.0- 96.0[4]	38.5[3]
8-	50.5-51.2	44.9	8, 9-	117.0-117.7	43.6	8, 9-	95.0- 95.6	45.6
9-	43.7-43.9	49.0	9,10-	130.7-131.0	41.8[c]	9,10-	94.7- 95.1	39.1
10-	52.0-52.6[4]	45.5[6]	10,11-	120.0-121.0[4]	43.9[5]	10,11-	98.0- 99.5[4]	45.5[5]
11-	43.5-44.1	49.0	11,12-	127.5-128.0	41.8[c]	11,12-	92.5- 93.0	39.0
12-	52.0-53.0[4]	45.5[6]	12,13-	119.0-120.0[4]	43.9[5]	12,13-	96.0- 97.0[4]	45.5[5]

[a] Prepared from *trans*-octadecenoic acids by hydroxylation with performic acid.
[b] Prepared from *cis*-octadecenoic acids by hydroxylation with performic acid.
[c] These have the same long-spacing but the intensities for a given order vary from compound to compound.

TABLE II

Melting Point and X-Ray Diffraction Data on 50:50 Binary Mixtures

Trans-Octadecenoic Acids			High-Melting Dihydroxystearic Acids			Low-Melting Dihydroxystearic Acids		
	M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å
6- + 8-	44.6-46.1	38.9[a]						
7- + 9-	36.7-38.0	46.0[a]	7, 8- + 9,10-	118.0-121.6	....[c]			
7- +11-	34.5-35.7		7, 8- +11,12-	117.0-122.0	....[c]			
9- +11-	36.6-37.7	46.0[a]	9,10- +11,12-	116.5-122.0		9,10- +11,12-	83- 85	45.6[d]
6- + 7-	37.8-43.8		6, 7- + 7, 8-	115.0-123,0	....[b]			
6- + 9-	37.2-43.2	....[b]	6, 7- + 9,10-	111.0-123.0	....[b]	6, 7- + 9,10-	87-110	45.6[d]
7- + 8-	37.2-42.8	....[b]	7, 9- + 8, 9-	111.0-123.0	....[b]	6, 7- +11,12-	88-106	45.6[d]
8- + 9-	36.2-41.2	....[b]	8, 9- + 9,10-	110.0-122.5	....[b]	8, 9- + 9,10-	79- 85	45.6[d]

[a] A one-phase system was obtained different from that of either pure component.
[b] The diffraction patterns were the combined pattern of the two pure compounds.
[c] Long spacings are equal to the identical values of the two components and intensities of the various orders appear to be a summation of the corresponding intensities of the pure components.
[d] These have the same long spacing but the intensities for a given order vary from mixture to mixture.

---

[1] This note is XIX in the series Reactions of Fatty Materials with Oxygen. The previous paper is Reference (1).
[2] Eastern Regional Research Laboratory.
[3] The Ohio State University. Present address for Mr. Fusari: Parke, Davis and Company, Detroit, Mich.
[4] One of the laboratories of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

diffraction pattern offers a simple explanation for this. Mixtures of even-even or odd-odd acids form a one-phase system; mixtures of odd-even form a two-phase system and give diffraction patterns in which those of the pure components are superimposed.

Similar results are obtained in the melting points of the dihydroxystearic acids. Binary mixtures (50:50) of the dihydroxystearic acids from odd-odd or even-even octadecenoic acids have melting ranges from 2-5° whereas those from odd-even acids have melting ranges from 6-18°.

REFERENCES

1. Coleman, J. E., and Swern, Daniel, J. Am. Oil Chemists' Soc., *32*, 221–224 (1955).
2. Fusari, S. A., Greenlee, K. W., and Brown, J. B., J. Am. Oil Chemists' Soc., *28*, 416-420 (1951).
3. Hellman, N. N., and Senti, F. R., paper presented at American Oil Chemists' Society meeting, New Orleans, La., May 1-3, 1951.
4. Huber, W. F., J. Am. Chem. Soc., *73*, 2730-2733 (1951).
5. Lutton, E. S., Huber, W. F., Mabis, A. J., and Stewart, C. B., J. Am. Chem. Soc., *73*, 5206-5210 (1951).
6. Lutton, E. S., and Kolp, D. G., J. Am. Chem. Soc., *73*, 2733-2735 (1951).
7. Swern, Daniel, Billen, G. N., Findley, T. W., and Scanlan, J. T., J. Am. Chem. Soc., *67*, 1786-1789 (1945).
8. Swern, Daniel, and Scanlan, J. T., Biochemical Preparations, *3*, 118-120 (1953).
9. Witnauer, L. P., and Swern, Daniel, J. Am. Chem. Soc., *72*, 3364-3368 (1950).

[Received March 25, 1955]

ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
Sin'itiro Kawamura, Abstractor

Component Fatty Acids of Indian Snake Oils. Y. D. Karkhanis and N. G. Magar (Dept. Biochemistry, Institute of Science, Bombay 1, India). *Biochem. J.* **60**, 565–8 (1955). The component fatty acids of the oils of two Indian snakes, *Python molurus* and *P. stinotis*, were studied. The following fatty acid percentages were found, with the first value that of *Python molurus* and the second value that of *P. stinotis*: myristic, ..., 1.6; palmitic, 16.1, 15.7; stearic, 10.1, 13.3; arachidic, 2.3, 1.0; tetradecenoic, ..., 0.2; hexadecenoic, 4.8, 5.2; octadecenoic, 41.3, 36.8; octadecadienoic, 7.6, 9.4; octadecatrienoic, 3.0, 3.2; eicosenoic, 11.9, 12.8; eicosatetraenoic, ..., 0.8; and docosenoic, 3.0, ...

Extraction technique in cottonseed oil processing. M. Pilette. *Oleagineux* **10**, 303–308, 399–407, 495–500 (1955). Commercial methods and equipment for preparing the seeds, recovering the oil by pressing and purifying the crude cottonseed are reviewed. The nutritive value of the press cakes and the influence of the various extraction processes on the quality of the products also are considered.

Viscosimetry of vegetable oils. II. Kinematic viscosity of mixtures of olive oil with n-butanol, isoamyl alcohol, and cyclohexanol at different concentrations and temperatauures. P. Klantachnigg *Olearia* **9**, 105–113 (1955). Kinematic viscosity studies were made on mixtures of olive oil in *n*-butanol, isoamyl alcohol and cyclohexanol at temperatures of 10–80°. The mixing of olive oil with *n*-butanol or isoamyl alcohol gave no appreciable variation in volume over that of the added oil. With cyclohexanol there was a volume increase greater than that of the added oil. The addition of small quantities of oil to *n*-butanol and isoamyl alcohol gave much smaller changes in viscosity than the addition of small quantities of the alcohols to the oil. Such variations in viscosity diminished noticeably as the temperature was increased. Mixtures of oil with cyclohexanol showed the phenomenon of negative viscosity which decreases as the temperature is raised until it disappears above 60°. The Walther equation for viscosity-temperature relationships was found to be applicable to mixtures of the oil with the three solvents when a constant, calculated additively from that of the oil and that of solvent, was introduced.

The oil from the seeds of Hippophae Rhamnoides L. I. Study of the fatty acids. H. P. Kaufmann and A. Vazquez Roncero. *Grasas y Aceites* **6**, 81–87 (1955). Finely pulverized seeds of *Hippophae Rhamnoides L.* were Soxhlet extracted with hexane to give 6.4% of an intensely red oil. The oil contained 2.1% of unsaponifiables (petroleum ether method) and had an acid number of 5.97, a saponification number of 186.8, an iodine value of 152.3, a thiocyanogen value of 100.2, a hydroxyl value of 11.9, and contained 93.8% of total fatty acids. Chemical constants also were determined for the total acids recovered from the saponification of the oil. From these values it was calculated that the total fatty acids contained 11.6% of saturated acids, 26.6% oleic acid, 34.7% linoleic acid, 27.0% linolenic acid and no tetra-unsatruated acids. Spectrophotometric studies gave results of about the same order except that 1.74% of a tetra-unsaturated acid was detected. Qualitative paper chromatography studies indicated that the saturated acids consisted of palmitic and stearic acids only.

II. Study of the unsaponifiables. *Ibid.*, 129–134 (1955). The unsaponifiables were recovered in the usual way from the oil by saponification and ether extraction with all operations being carried out under an inert atmosphere. The carotinoids were separated by chromatography on alumina and the various fractions were studied by absortion spectra. Zeaxanthin, cryptoxanthin, β-carotene, γ-carotene and probably lycopene were detected. Quantitative studies showed the presence of 58.1 mg. of zeaxanthin, 64.8 mg. of cryptoxanthin, and 8.7–9.8 mg. of β-carotene per 1,000 grams of oil. The sterols were isolated from the unsaponifiables as the digitonides and by 0° crystallization of a methanolic solution of the unsaponifiables. The sterols were characterized as sitosterols by formation of the bromides and acetates.

Study on the oils from the hulls of Tunisian olives. M. R. Fuhrmann. *Revue Francaise des Corpus Gras* **2**, 237–256 (1955). Samples of the oil from the hulls of Tunisian olives were saponified, the unsaponifiables extracted with ethyl ether and the fatty acids recovered from the soap solution in the usual manner with all operations being conducted under an atmosphere of nitrogen. The total fatty acids made up 94% of the oil, while the unsaponifiables amounted 2.0–2.5%. The acids were separated into two fractions by crystallization from acetone at −28° with the precipitated fraction being recrystallized twice from the same solvent. Each of the acid fractions was converted separately into the methyl esters which were distilled under vacuum. The unsaponifiables were separated into a number of fractions by chromatography on alumina and crystallization. Characterization studies were conducted on all fractions. The fatty acid fractions were made up of the following acids: myristic (0.7%), palmitic (13.9%), stearic (1.9%), saturated acids containing more than 20 carbon atoms (0.9%), palmitoleic (1.6%), oleic (64.0%), linoleic (15.1%) and unsaturated acids containing more than 20 carbon atoms (2.1%). Chlorophyll decomposition products amounting to 0.03–0.04% of the whole oil also were recovered from the saponifiable fraction. Hydrocarbons isolated from the unsaponifiables made up 0.50 to 0.66% of the whole oil and contained straight chain paraffins of an average molecular weight of C_{29}–C_{31}, squalene (0.17–0.22% of the oil) and a mixture of at least 4 hydrocarbons, one of which showed an intense blue fluorescence. Sterols also were present in the unsaponifiables and made up 0.48–0.54% of the oil. These consisted of β-sitosterol, provitamin D and an uncharacterized dextrorotary sterolic fraction with a melting range of 164–167°. A mixture of at least three straight chain fatty alcohols (0.20–0.30% of the oil) in the range C_{24}–C_{28} was present in the unsaponifiables as well as an amorphous transparent dextroratory resinous fraction which amounted to 1% of the oil and contained hydroxyl groups which could be acetylated. The remainder of the unsaponifiables consisted of carotenoid pigments.

Tall oil comes of age. Anon. *Paint Oil Chem. Review* **118** (15). 10 (1955). Tall oil is defined, and the production and economics are discussed.